

The University of Chicago

CATALYTIC EFFECTS IN
THE BROMINATION OF TOLUENE

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1938

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PHILIP C. WHITE

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I. CATALYTIC EFFECTS IN THE BROMINATION OF TOLUENE

Introduction

Many investigators have studied the various aspects of the bromination of toluene. A thorough review of their findings reveals little more than a maze of disconnected and frequently discordant facts. The action of catalysts and solvents, and the effects of light, temperature, and concentration have all been subject to careful attention. Many theories have been proposed to explain these observations, and while each theory is supported by some phase of the data, there is none which satisfactorily correlates all of the experimental work.

We have found that traces of organic peroxides strongly catalyze the substitution of bromine in the side-chain of toluene. Such peroxides, on reaction with hydrogen bromide, are assumed to produce bromine atoms.¹ Furthermore light, which exerts the same effect on side chain bromination as does peroxide, is known to dissociate the bromine molecule into atoms. Hence, in an effort to correlate this new observation with previous work, we were led to the hypothesis that the reagent responsible for the substitution of bromine in the methyl group of toluene is the bromine atom, and that once such atoms are produced in solution, bromination can continue by a chain mechanism.

It is the purpose of this thesis to show that earlier experimental work can be satisfactorily explained in the light of this mechanism, and that the hypothesis is substantiated by the data obtained in this investigation.

Review of the Literature

One of the first points which received the attention of early workers studying the bromination of toluene was the complete independence of the two possible substitution reactions. The bromine can enter the methyl group to give benzyl bromide, or can take either the ortho or para position in the ring to give a bromotolu-

¹Kharasch, Engelmann and Mayo, J.Org. Chem., 2, 298 (1937).

ene. These are two separate reactions and their relative rates vary widely with the experimental conditions.² Obviously any change in one rate relative to the other will alter the ratio of the products.

Normally these are the only products formed. Meta-bromotoluene, as has been established by careful search, is only formed in very concentrated solution and in the presence of a catalyst.³ Even then, the yield is only a fraction of one per cent. Likewise, polybrom compounds are not formed except in the presence of a large amount of catalyst, such as thirty mole per cent aluminum,⁴ or beryllium bromide.⁵

Catalysts exert a strong influence on the direction of bromine substitution in toluene. In general the catalytic effects may be divided into two classes. Metals, metal halides and iodine increase the rate of nuclear substitution, while light and ozone promote substitution in the side-chain. Aluminum bromide seems to be the most effective carrier. At 50°C. as little as 0.4 mole per cent aluminum bromide on the basis of the bromine raises the yield of bromotoluene from 46 per cent to 99.5 per cent.⁶ To produce such an effect with iodine at 25°C. requires 5 mole per cent.⁷ The photobromination, even in diffuse light, gives 98 per cent benzyl bromide, and is complete in a few minutes, while reaction in the dark requires many days.⁸ Ozone has an effect similar to light, greatly accelerating the side-chain reaction.⁹ It appears to be a general rule that when benzyl bromide is the predominant product the reaction is an extremely rapid one, while nuclear substitution is by comparison quite slow. Such a difference is to

²Van der Laan, Rec. trav. chim., 26, 1 (1907).

³Holleman, ibid., 33, 183 (1914).

⁴Van der Laan, op. cit.

⁵Pajeau, Compt. rend., 202, 1795 (1936).

⁶Van der Laan, op. cit.

⁷Bruner and Dluska, Bull. Acad. Sci. Cracow, 1907, 691.

⁸Van der Laan, op. cit.

⁹Bruner and Lahocinski, Bull. Acad. Sci. Cracow, 1910,

be expected between a bimolecular reaction and a chain mechanism involving bromine atoms. The chain reaction involves unstable reactive intermediates. It must proceed rapidly or not at all.

Temperature exerts a strong influence on the direction as well as the rate of the bromination reaction. Regardless of other factors such as concentration and catalysts, it is uniformly true that the higher the temperature, the higher the yield of benzyl bromide.¹⁰

The effect of the bromine concentration upon the ratio of the two products when no solvent or catalyst is used, was first observed by Bruner and Dluska,¹¹ and later studied by Holleman.¹² The more dilute the solution the higher is the relative yield of benzyl bromide. The effect appears at all temperatures studied. By a proper combination of temperature and concentration it is possible to obtain almost any desired ratio in the products, as is shown by the results of Holleman, given in Table 1. These reactions were carried out at 50°C. in darkness, and were allowed to proceed to completion. At very high dilution, 100:1 or greater, and at elevated temperature the product is 100 per cent benzyl bromide.

TABLE 1
THE EFFECT OF DILUTION UPON THE RATIO OF
SUBSTITUTION PRODUCTS

Mole Ratio: Toluene/Bromine	Percentage of Benzyl Bromide in the Product
4.3	24
8.0	42
10.4	56
20.6	82
28.5	95

The dependence of the type of substitution upon concentration indicates that diminishing bromine concentration will change the direction of substitution during the course of the reaction. Thus, the final ratio of the products will depend upon the point

¹⁰Van der Laan, op. cit.

¹¹Bruner and Dluska, op. cit.

¹²Holleman and Polak, Rec. trav. chim., 27, 435 (1908).

at which the reaction is stopped. Failure to recognize this fact caused considerable disagreement among the early workers. Holleman's reactions went to completion. Hence his results do not show, as do those of Bruner, the interesting fact that while the rate of nuclear substitution falls off normally with increasing dilution, the rate of substitution in the side-chain is actually faster in more dilute solution.¹³ This would be expected if bromine molecules in some way hindered the side-chain substitution. Such a process can easily be correlated with the theory of a chain reaction for this substitution reaction. The bromine molecules act as "chain breakers" by combining with the bromine atoms. Hence, the rate of substitution in the methyl group decreases with increasing concentration of bromine.

Bruner and his coworkers also gave careful attention to the effect of various solvents on the bromination of toluene, both in the light and in the dark. For the dark reaction the results set forth in Table 2 illustrate the general effects they observed.¹⁴

TABLE 2
THE EFFECT OF SOLVENTS ON THE BROMINATION OF TOLUENE*

Solvent	Time (Days)	Percentage of Bromine Substituted	Percentage of Benzyl Bromide in Product
Carbon disulfide.....	33	38	82
Carbon tetrachloride..	30	48	50
Benzene.....	30	73	38
Acetic acid.....	5.5	61	4
Nitrobenzene.....	1	92	3

*The toluene/bromine ratio was 10:1, and the solvent was added to give a volume equivalent to a toluene/bromine ratio of 40:1.

They call attention to the direct relation between the ionising power of the solvent and its effect in catalysing nuclear and in inhibiting side-chain substitution. Although carbon disulfide and carbon tetrachloride act merely as inert diluents, acetic acid and

¹³Bruner and Dluska, op. cit.

¹⁴Bruner and Vorbrod, Bull. Acad. Sci. Cracow, 1909, 221.

nitrobenzene have pronounced effects. Similar influences prevail in the photobromination where acetic acid and nitrobenzene retard the rate of reaction and lower the yield of benzyl bromide to about 70 per cent.

A brief outline of the various theories proposed for this single factor of the solvent effect will serve to show the general confusion existing in this field. Holleman explains these results by the relative solubility of hydrogen bromide in the various solvents,¹⁵ but while his data for acetic acid solution demonstrate the inhibition of the side-chain substitution by hydrogen bromide, they do not establish any positive catalytic effect on nuclear substitution. LeBlanc and Andrich attempt to correlate these data on the basis of the difference in solvation in associating solvents, such as toluene and ethyl acetate.¹⁶ This, they claim, decreases the photosensitivity of the bromine and hence inhibits side-chain substitution. However, this interpretation fails to explain the effect of solvents on the yield of bromotoluene. Lauer and Oda attempt to explain the increased yield of bromotoluene by assuming that the ionoid character of the ring is raised (with a corresponding increase in reactivity) because of the greater association of the toluene molecule in such solvents.¹⁷ However, experimental facts do not support this hypothesis. It is argued that since association presumably takes place through the methyl group, it blocks any substitution in the side-chain. One might expect therefore that the more dilute the solution of toluene in the solvent, the less would be the degree of its association and that higher rather than lower yields of benzyl bromide would be obtained. In this connection see Table 6, Experiments #26 and #27.

The "after effect" found by Bruner is very significant in the light of our work on the catalysis by peroxides. He reports that when photo-bromination occurs, a catalyst is produced which upon addition of more bromine causes a very rapid reaction in the dark with the formation of 90-95 per cent benzyl bromide.¹⁸ Oxygen

¹⁵Holleman and Polak, op. cit.

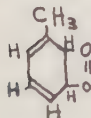
¹⁶Andrich and LeBlanc, Z. wiss. Phot., 15, 148, 153, 197 (1916).

¹⁷Lauer and Oda, Ber., 69B, 984, 1062 (1936).

¹⁸Bruner and Lahocinski, op. cit.

is absorbed during the formation of the catalyst and the solution takes on a yellow color. Replacement of the dissolved oxygen, before illumination, by carbon dioxide, hydrogen, or nitrogen prevents the occurrence of the effect, as does the addition of iodine or hydrogen bromide after the photobromination. Since such a catalyst is not produced on illuminating a solution of toluene, benzyl bromide and hydrogen bromide, bromine is apparently necessary. The more dilute the bromine solution during the "after-effect," the greater is the influence of the catalyst. It is apparently destroyed or ineffective in very concentrated bromine solutions.

Further work on this "after-effect" shows that this catalyst liberates iodine from potassium iodide.¹⁹ An attempt to isolate the catalyst yielded a small amount of material with a "phenol and cresol-like" odor. LeBlanc and Andrich assume the catalyst to be some sort of peroxide. Since its formation is found to occur on exposure to the visible region of the spectrum, where neither toluene nor oxygen absorb, it must be the bromine which renders the formation light-sensitive. They cite this property of bromine as one established in other photo-chemical reactions.²⁰ As to the mode of action of the catalyst, however, their only suggestion is the formation of an intermediate such as the compound:



This would account for the low yields of nuclear products and the yellow color, but not the greatly accelerated side-chain substitution. In view of our findings, this peroxide probably acts as do others to produce bromine atoms and to set up chain reactions

for substitution in the methyl group.

Oxygen itself is well-known to be involved in the ordinary photochemical reaction, but the fact seems to have received little attention. LeBlanc and Andrich found that by working in an atmosphere of oxygen their yields of benzyl bromide were slightly higher and were more nearly reproducible than when the reaction was carried out in air.²¹ Bruner observed that removal of oxygen by evacuation or replacement by an inert gas retarded the photobromi-

¹⁹Andrich and LeBlanc, op. cit.

²⁰Bruner and Krolikowski, Bull. Acad. Sci. Cracow, 1910, 192.

²¹Andrich and LeBlanc, op. cit.

nation but he never analyzed the products to determine what effect this treatment might have upon the direction of the reaction.²² Furthermore, in the dark, in highly dilute solution, he observed an autocatalytic rate which depended upon the presence of oxygen for its existence. In this case the reaction produced 100 per cent benzyl bromide, while the slower reaction, in the absence of oxygen, gave only 80-90 per cent benzyl bromide.

In summarizing the various factors which have been found to affect the reaction, one can make the following division. Substitution in the side-chain is favored by dilution, high temperature, oxygen and ozone, light and some peroxide-like substance formed on exposure to light. Nuclear substitution, on the other hand, is catalysed by metal halides, iodine, and certain ionizing solvents. We shall now discuss a few of the theories which have been evolved in attempting to postulate a satisfactory mechanism for the substitution reaction. We shall show where they fail, and how the hypothesis presented in the Introduction constitutes a simple and satisfactory explanation of the facts.

Discussion of Mechanism

It was recognized from the time of the earliest work on this problem that the two independent substitution reactions must necessarily proceed by different mechanisms. If this were not the case one would expect various factors to affect both reactions similarly. This difference was noted first in the case of the metal halide catalysts. It was originally assumed that these acted through "active" complexes such as $\text{FeBr}_3 \cdot \text{Br}_n$. However, Bancroft pointed out that such an "active complex" might stimulate the side-chain as well as ring substitution.²³ It is now the consensus that the halogen carriers activate the hydrocarbon ring rather than the bromine molecule.

In the case of the uncatalysed bromination of toluene it was suggested that the mechanisms differed as to the reagent actually involved in the substitution. Holleman postulated that " HBr_n " attack the nucleus, while bromine molecules cause substitution in the chain. This hypothesis agreed with his work in

²²Bruner and Czarnecki, Bull. Acad. Sci. Cracow, 1910, 516.

²³Bancroft, J. Phys. Chem., 12, 417 (1908).

acetic acid in which hydrogen bromide decreased chain substitution. Also according to this hypothesis the temperature effect is due to the decomposition of the complex HBr_n by heat; hence the side-chain substitution is left as the predominant reaction. However, Holleman himself recognized the failure of the theory to explain the dilution effect. At the beginning of the reaction no hydrogen bromide is present in the mixture, yet in concentrated bromine solution nuclear substitution proceeds very rapidly even in the absence of " HBr_n ."

Bruner arbitrarily suggests the bromine atom as the reagent for nuclear substitution, but he offers no evidence in confirmation of such a theory. LeBlanc and Andrich ascribe the temperature effect to the decrease in solvation of the bromine molecule, but they go no further in applying their theory to other phases of the reaction.

Let us examine how the "bromine atom" hypothesis explains these diverse observations. It postulates that bromine atoms substitute in the methyl group, and that once started this substitution proceeds by a chain reaction. Such a mechanism can be affected in two ways. Factors inhibiting the chain reaction will retard side-chain substitution, and factors raising the number of bromine atoms present (the number of chains initiated) will obviously increase this reaction rate. Let us examine these factors in greater detail.

A few bromine atoms will exist in the toluene solution merely by virtue of the thermal dissociation of the bromine molecules. A rise in temperature will increase this dissociation. If the heat of dissociation is assumed to be in approximately 46,000 calories the concentration of bromine atoms will be a hundred times greater at 80°C . than it will be at room temperature. Hence, we should expect to find a rather large positive temperature coefficient for this reaction. Bruner's work shows that the temperature coefficient for substitution in the side-chain is over four times as large as that for nuclear substitution.²⁴ To some extent a change in concentration would also affect the degree of dissociation of the bromine molecule according to the Mass Law. While this effect would give more bromine atoms in more dilute solution, it is doubtless too small to be of much significance.

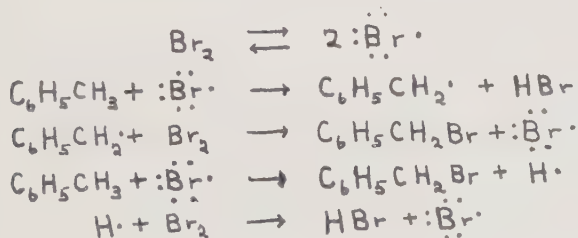
²⁴Bruner and Dluska, op. cit.

If the reaction between oxygen and hydrogen bromide is capable of producing bromine atoms,²⁵ then Bruner's discovery at high dilution, that oxygen produces an auto-catalytic increase in the rate of reaction, is explained simply by the increase in hydrogen bromide concentration as the reaction proceeds. This phenomenon appears only at a dilution such that the formation of benzyl bromide is the principal reaction and the amount of available oxygen is comparatively large. If the interaction of oxygen with hydrogen bromide gives bromine atoms, then peroxides and ozone should be still more active in this reaction. This explains the very strong catalytic effect these substances have in the formation of benzyl bromide.

Light has long been recognized as a means of producing bromine atoms, but apparently under the conditions of the reaction it can also act indirectly. As shown above, work on the "after-effect" indicates that light sensitizes oxygen to form some sort of peroxide in the reaction mixture. It also may sensitize the direct reaction between hydrogen bromide and oxygen in a manner observed in the addition of hydrogen bromide to unsaturated compounds.²⁶

Hence it can be seen that oxygen, peroxides, light, and heat each act on a reaction mixture of bromine and toluene to increase the number of bromine atoms present. As indicated above each of these factors also increases the rate and extent of side-chain substitution. The effect of concentration and solvents comes under the category of factors influencing the chain length.

The chain reaction is thought to involve the following reactions:



²⁵Kharasch, Engelmann and Mayo, op. cit.

²⁶Kharasch and Mayo, J. Am. Chem. Soc., 55, 2468 (1933).

Once started this chain will continue until broken by some other reaction. Since the bromine molecule can act as a chain-breaker, it is obvious that in concentrated bromine solutions the chain length will be relatively short and the yields of benzyl bromide correspondingly low. Likewise certain solvents, because of their chemical nature, can act as inhibitors for the chain reaction.

The proposed hypothesis therefore merits consideration merely because it offers a simple explanation of the experimental facts. While it leaves the matter of nuclear substitution unsettled, there are no observations not in accord with the theory that the nuclear reaction is bimolecular. Moreover, the adoption of the hypothesis enables one to make certain predictions which follow logically from the mechanism proposed. If small traces of peroxides act by initiating chain reactions (a chain reaction is the most reasonable explanation for homogeneous catalysis) substances which break the chains should be effective in equally small amounts. Hence one would anticipate very effective inhibition of the chain reaction by certain compounds. By the same reasoning peroxide catalysis should be decreased in concentrated bromine solutions, and should be at a minimum in certain solvents. Furthermore, if light can act indirectly when oxygen is present to produce bromine atoms, the removal of oxygen should decrease the yield of benzyl bromide in the photochemical reaction. The results which follow show these predictions to be correct, and in so doing substantiate the proposed hypothesis.

Discussion of Results

The dilution effect.--The addition of a small amount of an organic peroxide to a mixture of toluene and bromine in the dark increases the rate of reaction greatly and raises the yield of benzyl bromide. The effectiveness of this catalyst is, however, inversely related to the concentration of the bromine, and in very concentrated solutions the effect almost vanishes. Furthermore, the peroxide is more effective if added slowly during the course of the reaction. Benzoyl peroxide, ascoridole, and tri-acetone peroxide have all been found to have this catalytic action. Table 3 gives the results of a series of experiments with and without peroxide at various dilutions and reaction times. While a comparison of the various control experiments confirms the observa-

TABLE 3
PEROXIDE CATALYSIS AT VARIOUS DILUTIONS

No.	Mole Ratio Toluene/ Bromine	[Peroxide] in Mole Per Cent	Time (Hours)	Net Yield in Per Cent	Estimated Yield in Per Cent		
					Total	Benzyl Bromide	Bromo- toluene
1	2	0	23	72	89	1	88
2		0	0.75	38	47	0.3	47
3*		3	23	64	82	4	78
4*		3	0.75	37	47	4	43
5	5	0	23	48	58	2	56
6*		3	23	53	65	17	48
7	10	0	96	61	75	7	68
8*		0	23	14	22	1	21
9*		3	23	67	94	85	9
10*		3	5	79	94	89	4
11		3	0.06	73	90	87	3
12	20	0	91	25	33	11	22
13		0	48	15	22	8	14
14		3	0.5	85	100	95	5
15		(in vacuo) 0	91	21	30	10	20

*Indicates an average of two or more experiments. Same in following tables.

tions of earlier workers as to the dilution effect, the latter is shown much more strikingly in the case of the peroxide experiments. Here any variation in the initial concentration of the bromine atoms due to dissociation is eliminated as hydrogen bromide and peroxide produce them in far greater numbers. The wide variation in yield of benzyl bromide can only be due to the interruption of the chain reaction which occurs in concentrated solution.

Since the life of a bromine atom in such solutions must be extremely short, and the peroxide present is rapidly destroyed in forming atoms, one would expect any chain reaction involving them to be extremely rapid. A comparison of the benzyl bromide yield in experiments #9 and #11 shows clearly that the reaction initiated by the peroxide has run its course within a few minutes. However, in the control experiments in dilute solution, where the initial bromine atoms can only come from dissociation, this furnishes a continual, if very minute, supply, and the yield of benzyl bromide increases uniformly with time as shown by experiments #7 and #8, or #12 and #13. The effect of oxygen as a source of bromine atoms in these control experiments is apparently insign-

nificant at 20:1 dilution (cf. #12 and #15), although Bruner indicates that it enters at 200:1 dilution.

The rate of nuclear substitution shows a uniform increase with increasing concentration. The data, however, are not sufficiently quantitative to warrant any kinetic interpretation which might throw light on the mechanism for bromination of the ring. One can say only that the data do not contradict an hypothesis of a bimolecular reaction for nuclear substitution, and they do demonstrate that nuclear substitution does not take place through a bromine atom mechanism.

The bromotoluene products from one control and one peroxide-catalysed experiment were analyzed by the freezing-point method of van der Laan²⁷ to determine whether the presence of peroxide during the reaction has any influence on the ortho to para ratio in the nuclear substitution product. Table 4 indicates that peroxides have no effect on the ortho para ratio. The ratio in each case was determined directly from the freezing-point curve given by van der Laan.

TABLE 4
EFFECT OF PEROXIDE ON THE ORTHO-PARA RATIO

Experiment	Time	Net Yield in Per Cent	Percentage of Benzyl Bromide	Freezing Point Bromo- toluenes	Percentage of Ortho- Bromo- toluene
Control... 3 mole per cent peroxide	4 days	61	10	-8°C	54
	1 day	68	90	-9°C	55

The action of inhibitors.--The complete inhibition of side-chain substitution by very small concentrations of certain substances supports a chain mechanism for the peroxide catalysed reaction. Several compounds containing the -N=O group have been found to have this effect, and to a much lesser degree ethyl alcohol.²⁸ Table 5 gives the results with a few such compounds, and includes the control experiments for comparison. Qualitative

²⁷Van der Laan, op. cit.

²⁸Swenson, Z. wiss. Photo-Chem., 20, 206 (1921).

tests showed many similar substances such as iso-amyl nitrite, p-nitroso dimethyl aniline, and even sodium nitrite to be effective inhibitors. This inhibition is not merely due to the binding or destruction of the peroxide by an equivalent quantity of inhibitor, since it also occurs in the photobromination. In the presence of a few mole per cent of iso-amyl nitrite the light catalysed reaction is complete only after many hours, whereas it normally requires only a few minutes. Water, acetic acid and nitrobenzene have no appreciable inhibiting action when present in small concentrations.

TABLE 5

EFFECT OF INHIBITORS ON THE PEROXIDE-CATALYSED REACTION^a

No.	Nature and Conc. of Inhibitor	[Peroxide] in Mole per Cent	Time (Hours)	Net Yield in Per Cent	Estimated Yield in Per Cent		
					Total	Benzyl Bromide	Bromo-toluene
8*	None	0	23	14	22	1	21
9*		3	23	67	94	85	9
10*		3	5	79	94	89	4
16	3 mole % ONNO	0	24	33	40	1	39
17*	3 mole % ONNO	3	24	33	44	1	43
18	3 mole % N_2O_4	3	23	16	24	1	23
19	2.6 mole % $\text{C}_2\text{H}_5\text{OH}$	0	23	50	67	0.5	66
20*	3 mole % $\text{C}_2\text{H}_5\text{OH}$	3	23	50	67	15	52
21	3 mole % H_2O	3	4	79	95	92	3
22	5 mole % HAc	3	24	78	94	82	12
23	5 mole % O-NO_2	3	24	83	98	85	13

^aToluene/bromine ratio is 10:1 in all experiments.

The solvent effect.--The use of solvents in the peroxide catalysed reaction, as shown in Table 6, merely confirms those observations already made.

Carbon tetrachloride is an inert diluent and decreases the rate of side-chain and nuclear substitution. Strikingly, however, acetic acid and nitrobenzene strongly inhibit the peroxide catalysed chain reaction. Note also that the rate of nuclear substitution is increased. This effect may be due to the higher dielectric constants of these solvents as well as the suppression of side-chain bromination. Experiment #29 shows that hydrogen

TABLE 6

THE EFFECT OF SOLVENTS ON THE PEROXIDE CATALYSED REACTION

No.	Solvent Added to Give Volume = 10:1 Ratio	Mole Ratio Toluene/ Bromine	[Peroxide] in Mole Per Cent	Time (Hours)	Net Yield in Per Cent	Estimated Yield in Per Cent		
						Total	Benzyl Bromide	Bromo- toluene
8*	None	10	0	23	14	22	1	21
9*	None	10	3	23	67	94	85	9
24	CCl ₄	2	0	24	11	14	0.5	13
25*	CCl ₄	2	3	23	26	33	25	8
26	Acetic acid	1	0	23	29	36	0.5	35
27	Acetic acid	2	0	23	32	42	0.4	42
28	Acetic acid	2	3	23	32	40	1	39
29	Acetic acid	2	(97 mole % HBr)	23	15	19	0.2	19
30	Nitrobenzene	2	3	23	95	95	2	93

bromide cannot account for the catalysis of nuclear substitution. Also the association theory of Lauer and Oda, mentioned above, is refuted by Experiments #26 and #27 where the yield of benzyl bromide is not affected (within experimental error) by the change in concentration of the toluene.

The action of light.--It has been indicated that in the photobromination of toluene, light can act on two ways. By dissociating bromine molecules it can act as a constant initiator of chain reactions. The more dilute the solution the longer these chains will be. Furthermore, as long as there is oxygen present light can act indirectly to produce bromine atoms either by the actual formation of peroxides, or by catalysing the direct oxygen-hydrogen bromide reaction. Removal of the dissolved oxygen should cancel this indirect effect. The analysis of the products obtained in experiments in which the oxygen has been rigidly excluded shows the relative importance of the indirect effect. While both direct and indirect reactions produce bromine atoms and hence benzyl bromide, the retarding of one will give the simultaneous nuclear substitution a greater chance and will therefore result in a higher yield of bromotoluene. Table 7 gives experiments at dilutions of 10:1 and 5:1 including a "peroxide experiment" in the dark.

TABLE 7

THE OXYGEN EFFECT IN THE PHOTOBROMINATION

No.	Mole Ratio Toluene/ Bromine	Air	Light (100 Watts at 12 in.)	[Peroxide] in Mole per Cent	Time (Hours)	Net Yield in Per Cent	Estimated Yield in Per Cent		
							Total	Benzyl Bromide	Bromo- toluene
31	5	+	+	3	0.3	83	100	90	10
32	5	+	+	0	2.5	84	100	75	25
33	5	-	+	0	57.0	79	95	15	80
11	10	+	-	3	0.06	73	90	87	3
34	10	+	+	0	0.3	94	100	90	10
35	10	-	+	0	24.0	95	100	68	32

At 10:1 dilution the yield of benzyl bromide is lowered by removing the oxygen. It is interesting to note that the rate of bromination is also markedly decreased (24 hours in vacuo as compared with 20 minutes in air). In Experiment #35 bromine atoms are apparently being produced by the action of light on the bromine molecules, since the product is principally benzyl bromide, yet the slow reaction indicates that the number of atoms thus produced is very small compared to the number produced by peroxides. A still more marked oxygen effect is observable in the 5:1 dilution experiments. Here the nuclear substitution is predominant since the high bromine concentration inhibits the chain reaction. In the absence of oxygen the yield of benzyl bromide is only 15 per cent, and the rate of reaction is extremely slow, while in the presence of air over 70 per cent benzyl bromide is formed in a few hours.

These results lead one to reconsider the extent to which the direct photochemical dissociation of the bromine molecule is actually involved in the photobromination reaction. The materials used in these experiments were carefully degassed and the reaction tubes were evacuated to 10^{-5} mm. However, no attempt was made to remove the oxygen layer absorbed on the glass, and traces of oxygen are necessarily present even after the best evacuation. The fact that under these conditions only 15 per cent of benzyl bromide was formed after fifty-seven hours illumination (Expt. #33), indicates the possibility that if no oxygen were present, light might be without effect on the reaction. The experimental data

given herein do not prove this to be the case; indeed it may not be susceptible of proof. However, the data do not fail to prove the converse of this, i.e., that light does have a direct effect on the reaction independent of the presence of oxygen. It may be that in solutions of these concentrations light produces very few bromine atoms except through the activation of small amounts of oxygen. An alternate explanation of this oxygen effect may be that oxygen combines with some "chain-breaker" which otherwise is free to inhibit the light sensitized reaction.

As confirmatory evidence that the differences shown in these experiments is due to oxygen, it is noteworthy that in the reactions in which air is present decoloration always starts at the surface and proceeds downward through the solution. On the other hand in the vacuum experiments decoloration proceeds simultaneously throughout the entire reaction mixture.

Hence in the photobromination of toluene the significant effect of light is perhaps not the activation of the bromine, but what is more important the activation of minute amounts of oxygen.

Experiments on ethyl benzene.--Several experiments were carried out with ethyl benzene. With this compound, at a 1:1 ratio of bromine to the hydrocarbon in the dark, only the nuclear substitution products are formed.²⁹ A strong peroxide effect was observed in this reaction also. With a dilution of 7:1 the results were as follows.

TABLE 8
PEROXIDE EFFECT IN THE BROMINATION OF ETHYL BENZENE

[Peroxide] In Mole Per Cent	Time (Hours)	Net Yield in Per Cent	
		Nucleus	Side Chain ^a
0	25	14	26
2	1.5	6	91

^aNo analysis was made to determine whether this was the α or β compound. By analogy with the photobromination product it is probably α .

²⁹Schramm, Ber., 18, 607 (1885).

Experimental Part

Materials.--Mallinckrodt's "Analytical Reagent" toluene was distilled through an eight-bell Snyder column. The fraction boiling at 109.5° - 110.3°C . at 749 mm. of mercury was stored over sodium and used directly. Commercial grade ethyl benzene was shaken with mercury for several days to remove the sulfur, then dried and distilled, b.p. 134.8° - 135.2°C . at 747 mm. Baker's C. P. bromine was used without further purification. One test experiment using bromine which had been carefully washed with alkali and permanganate, then dried and distilled from P_2O_5 , gave exactly the same results as those obtained with the commercial product. The peroxide used in all the quantitative experiments was ascaridole obtained from the Eastman Kodak Company. Other peroxides used were prepared in small amounts in the laboratory when not commercially available. The solvents were of the best reagent grade and were distilled immediately prior to use.

Apparatus.--The majority of the experiments were carried out in a 200 cc. four necked flask equipped with two 50 cc. dropping funnels, a mercury seal stirrer and a reflux condenser. This flask was partially immersed in a thermostat kept at 25.0°C . The whole apparatus was covered with several layers of glazed black cloth which permitted the manipulation of the stopcocks without exposure to light. On the rare occasions when it was necessary to examine the mixture during the course of the reaction this was done with the aid of a small flashlight.

Procedure.--The bromine and the ascaridole, the latter diluted with a few cubic centimeters of toluene or solvent, were admitted to the reaction mixture through the two dropping funnels. The bromine was let in at once while the peroxide solution was admitted intermittently over a period of five or ten minutes. The mixture was stirred during this period and the hydrogen bromide evolved passed through the condenser into a water trap. The bromine was measured volumetrically, 0.040 or 0.080 moles being used. In some of the control experiments where the reaction was allowed to run several days, the reagents were merely mixed in a large open test-tube in the dark and kept at room temperature.

With the exception of the photobrominations, where the solutions were illuminated until colorless, the reaction was inter-

rupted while bromine was still present. In most experiments a current of air was passed through the stirred solution for an hour at the end of the reaction to remove as much hydrogen bromide as possible and thus reduce the amount of washing necessary. The reduction of the remaining bromine was then accomplished with little or no exposure to light by pouring the reaction mixture into an excess of dilute sodium bisulfite solution in a covered separatory funnel. The organic phase was immediately washed with water until the washings no longer showed a precipitate with silver nitrate. In those experiments in which acetic acid was used as a solvent, carbon tetrachloride was employed to extract the product from the aqueous solution after the unreacted bromine had been destroyed. When the reaction was carried out in nitro-benzene, the extent of bromination was determined by titration of the remaining bromine. Since the solvent and products could not be separated by fractionation in this case, the analysis for benzyl bromide was carried out on an aliquot sample according to the method given below.

The excess toluene was removed from the washed product by distillation under 20-30 mm. pressure. The products themselves were then distilled at the same pressure using a small Claisen flask with a long indented side-arm. No effort was made to separate the bromotoluenes from the benzyl bromide. The boiling range of the products was from 70°-95°C. depending upon the composition and the exact pressure.

The "net yield" of bromination products given in the various tables is that calculated from the weight of the distillate. However, there is necessarily a certain amount of loss in the washing and distillation. Material being carried over as the excess toluene was removed would be principally the lower boiling bromotoluenes. Conversely any hold-back in the distilling flask would be the side-chain substitution product. This last factor is negligible since the residue, except when ascaridole was used, was only 0.1-0.2 g. This fact also attests to the absence of any higher bromination products.

The "Estimated Yields" were arrived at by a consideration of the yields obtained in the photobrominations which had gone to completion and of the loss found in the treatment of artificial mixtures. Both washing and distillation claim from 15-20 per cent as is indicated by experiments #32 and #33. In experiments where

the yield was very low the same loss by weight would be a much larger factor. However, the treatment of artificial mixtures indicated that the loss in purification of very small samples was only 25 per cent, and was about equally divided between bromotoluene and benzyl bromide. A 50:50 mixture of benzyl bromide and bromotoluenes, weighing 2.0 g., lost 0.5 g. upon washing and distillation, and the remaining material analyzed for 53.0 per cent benzyl bromide. Hence the "Net Yields" were estimated as actually being 10-25 per cent too low, depending on the amount of reagents used in the individual experiment. The accuracy of the "Estimated Yield" is probably ± 10 per cent.

In the analysis for benzyl bromide a small weighed sample of the product was treated with an excess of standard silver nitrate in alcohol solution. Then the excess silver nitrate was determined according to the method of Volhard. All analyses were carried out in duplicate, and they consistently checked within 0.5 per cent. The balance of the product was assumed to be bromotoluene. The yields of benzyl bromide and bromotoluene were calculated directly from the results of this analysis and the Estimated Yield.

Experiments which were carried out in vacuo were performed in the following manner. The toluene and bromine were placed in separate tubes and these sealed on to a yoke on the vacuum line. To facilitate sealing there were constrictions in the tubing where the yoke joined line and where the tube containing the toluene was sealed to the yoke. Both tubes were chilled in liquid nitrogen, and the system was evacuated to a pressure of 10^{-5} mm. The yoke and the tubes were temporarily closed off by means of a stopcock above the constriction. Both reactants were warmed to their boiling point to permit the escape of dissolved gases. They were then chilled once more, the system re-evacuated, and this degassing process was repeated twice. The yoke and tubes were sealed off and the bromine distilled into toluene by allowing it to warm to room temperature. The reaction tube was then sealed off and was ready for illumination. The control reaction, in a sealed or open tube of the same diameter, was carried out simultaneously.

II. THE ADDITION OF BROMINE TO PHENANTHRENE

Discussion

A chain mechanism has been proposed³⁰ for the addition of bromine to phenanthrene, the principal evidence for such a mechanism being the strong inhibition of the reaction by very small amounts of certain antioxidants. Price also observed that benzoyl peroxide is without effect on the rate of addition. Since these findings have a direct relation to the theory concerning the bromination of toluene, outlined in the preceding paper, it became of interest to investigate the reaction of bromine with phenanthrene.

Experimental Results

Under conditions of total darkness no addition was found to occur even in twenty-four hours. However, upon the introduction of a small amount of ascaridole, reaction took place readily. The other peroxides tested were all much less effective than ascaridole, and unless the mixtures were allowed to stand many hours, no addition could be detected. Table 9 gives the results of these experiments, using carbon tetrachloride as a solvent. Price's observation that antimony pentachloride is a powerful catalyst, causing equilibrium to be reached rapidly in the dark, was confirmed.

As observed in the case of toluene, the effectiveness of the peroxide is decreased in concentrated bromine solution. This is in accord with the chain mechanism proposed, which is retarded by bromine molecules. However, an experiment at 0.01 moles per liter with three mole per cent ascaridole showed no addition, apparently being below the threshold concentration needed for reaction. Saturating the solution with hydrogen bromide before the addition of bromine had no effect, either in the absence or presence of peroxides.

³⁰Price, J. Am. Chem. Soc., 58, 1834, 2101 (1936).

TABLE 9

THE EFFECT OF PEROXIDES ON THE BROMINATION OF PHENANTHRENE
IN THE DARK

Concentration of Bromine and Phenanthrene (Moles/Liter)	Peroxide Employed	Concentration Total in Mole Per Cent	Time (Hours)	Extent of Reaction in Per Cent
0.5	None	-	1	0
0.5	Ascaridole	3	1	17
0.5	Ascaridole	10	1	92
0.05	None	-	24	0
0.05	Ascaridole	3	1	40, 40, 45
0.05	Tri-acetone peroxide	3	24	18
0.05	Benzoyl peroxide	3	24	45
0.05	Perbenzoic acid	3	24	29

These findings and the effects observed in the bromination of toluene indicated that oxygen has an important effect in this reaction. Table 10 shows the results of experiments carried out in vacuo and with different conditions of illumination. The

TABLE 10

THE EFFECT OF AIR ON THE PHOTOCHEMICAL BROMINATION OF
PHENANTHRENE

Reaction Time (Min.)	Conditions of Illumination		Extent of Reaction in Per Cent	
	Lamp Size	Distance	Control	Vacuum
24	400	15 in.	66	53
30	100	12 in.	62	41
40	100	24 in.	54	39
73 ^a	100	12 in.	59	24
50 ^b	400	15 in.	59	20

^aOne mole per cent diphenyl amine present in both reactions.

^bThe light was on only 30 seconds every five minutes.

photobromination of phenanthrene is faster in the presence than in the absence of oxygen. This difference is more marked when the illumination is intermittent, or when a small amount of anti-oxidant is present.

The extensive addition which occurs even with the reaction illuminated for very brief periods of time, comparable with the conditions imposed by the analytical method of Price, indicates that this worker was measuring the rate of a photochemical reaction. This explains why he reports a definite rate of addition even in the dark, a fact which cannot be confirmed in this laboratory. His failure to observe any effect from the relatively stable benzoyl peroxide is to be expected in a rapid light catalysed reaction. Price also states that no oxygen effect can be noted after boiling the solvent under diminished pressure. This is probably due to the traces of oxygen which are not removed by this method. The most careful evacuation, both before and during the reaction is often necessary to detect an oxygen effect.

These findings on the bromination of phenanthrene substantiate the theory that peroxides act by initiating a chain reaction which is carried by bromine atoms.

Experimental Part

Commercial "C. P." materials were used without further purification. In preliminary experiments the use of phenanthrene which had been purified according to the method used by Price, indicated that no inhibiting impurities were present in the unpurified C. P. reagent. The reaction was carried out in carbon tetrachloride solution, 25 cc. of the .05 M solution being the usual amount. In those experiments lasting only one hour the peroxide was added in four equal portions at fifteen minute intervals; otherwise it was all added at the start of the reaction. The analysis was by titration of the excess bromine with aqueous potassium iodide and standard sodium thiosulfate. The vacuum experiments were prepared as described in the previous paper, degassing the carbon tetrachloride and bromine before distillation into the reaction tube containing the phenanthrene. The concentration of the bromine and the phenanthrene was 0.05 moles per liter and each run was accompanied by a control reaction open to air. The evacuated tube was opened under potassium iodide solution from which the oxygen had been removed by boiling and saturating with nitrogen.

Thus the unreacted bromine was destroyed without exposure to oxygen.

SUMMARY

1. The work of various investigators on the bromination of toluene has been summarized and few of the mechanisms they propose for the reactions involved have been discussed.

2. A chain reaction carried by bromine atoms has been proposed as a likely mechanism for the bromination of the side-chain. It is in accord with the facts previously observed and is substantiated by the catalytic effects of peroxides under various conditions.

3. A strong oxygen effect has been observed in the photobromination of toluene, which influences the direction as well as the rate of the reaction.

4. Peroxides have been observed to catalyse the addition of bromine to phenanthrene in the dark.

5. Oxygen has an effect on the photobromination of phenanthrene, evacuation retarding the addition reaction.

6. These facts are in accord with the bromine-atom mechanism proposed for the bromination of toluene.

